

A geometrical model for Mixed cyanide crystals

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Abstract

A model of diluted random field sustained by quenched volume deformations is shown to reproduce puzzling physical features found in $X(CN)_xY_{1-x}$ mixed cyanide crystals. X is an alkali metal (K , Na or Rb) and Y is a spherical halogen ion (Br , Cl or I). Critical thresholds x_c at which associated first order ferroelastic transitions disappear are calculated exactly. The diluted random field is shown to compete with compressibility in making the transition first order. Transitions are then found to remain first order down to x_c except in the case of *bromine* dilution where they become continuous. All the results are in excellent agreement with available experimental data.

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1 Introduction

In recent years a great deal of experimental effort has been devoted to investigating the existence of a possible orientational glass state in mixed cyanide crystals [1, 2]. In particular diluted cyanide mixtures $X(CN)_xY_{1-x}$ where X is an alkali metal (K , Na or Rb) and Y stands for a spherical halogen ion (Br , Cl or I) are known to exhibit a series of puzzling physical features.

For instance, the ferroelastic transition which occurs in pure alkali-cyanides XCN [3] is found to disappear at a cyanide concentration threshold x_c which is not equal to the underlying lattice percolation threshold. The actual value of x_c varies with X and Y compounds. In the case $X = K$ it is $x_c = 0.60$ and $x_c = 0.80$ respectively for $Y = Br$ and $Y = Cl$.

In addition, below x_c there exists experimental evidence for local freezing of cyanide orientations, together with the absence of quadrupolar long range order. In parallel $X(CN)_xY_{1-x}$ mixtures remain cubic at low temperatures [1]. Analogies to spin-glasses and random field systems have thus generated much interest, in particular in elucidating the physical nature of the orientational glass state [1, 2].

Moreover the physics above x_c is still puzzling. The transition is found to be continuous at x_c for $X(CN)_xBr_{1-x}$ [4] while it stays first order with $X(CN)_xCl_{1-x}$ [5].

In this paper a model of diluted random field sustained by quenched volume deformations is proposed. It is shown to reproduce most of puzzling physical features found in $X(CN)_xY_{1-x}$ mixed cyanide crystals.

A derivation of a microscopic calculation of critical thresholds x_c is presented. On this basis, an Hamiltonian of a diluted compressible ferromagnetic Ising system is studied within mean field theory. Diluted staggered fields are then included to account for the quenched volume deformations generated by the substitution of spherical halogens to dumbbell-shaped cyanides.

Compressibility is found to produce a first order transition at cyanide concentrations larger than some threshold x_L . By contrast, diluted random fields are shown to activate a first order transition only below another cyanide concentration x_r .

Transition orders are then discussed for a large variety of mixtures. Relative amplitudes in x_c , x_L and x_r are instrumental in determining the transition order. Transitions are predicted to remain first order down to x_c for all mixtures except in the case of dilution with *bromine* which exhibits a continuous transition at x_c . Our results fit perfectly to available experimental data.

2 More than site dilution

Starting from pure XCN , substitution of one spherical molecule Y to a dumbbell-shape cyanide ion has first the effect of diluting one rotational degree of freedom. Within a simple site dilution picture, associated phase diagram would

be only slightly modified by dilution. The transition temperature would be a decreasing function of the “hole” (no degree of freedom) density. Moreover it would vanish at the lattice site percolation threshold. Here, it would mean ferroelastic transitions disappear at $x_c = p_c$ for all $X(CN)_xY_{1-x}$ mixtures where cyanides are on a fcc lattice where $p_c = 0.198$ [6]. However, from experiments $x_c \neq p_c$ and x_c varies from one system to another.

Several physical arguments can explain the discrepancy between x_c and p_c . Most of them like for instance the existence of long range interactions would lead one to give up the site dilution approach. However it could be kept allowing simultaneously an effective density of free-to-reorient cyanides. In other words, dilution would have the additional effect of “neutralizing” some cyanides taking them off the process of propagation of quadrupolar long range order active in the ferroelastic transition at stake.

The above picture is given a physical basis by postulating the existence of an effective density of free-to-reorient cyanides x_f , such that all ferroelastic transitions disappear at the same threshold $x_{f,c} = p_c$. It implies in parallel a density of “neutralized” cyanides x_n which depends on the mixture itself with $x_n = x_c - p_c$ at $x = x_c$.

At this stage we do not need to elaborate on the physics of these “neutralized” cyanides. What matters here is their non-participation in the propagation of long range order. The effect being a function of the mixture, we define naturally x_n as,

$$x_n \equiv \alpha(1 - x), \quad (1)$$

where α is the average number of cyanide “neutralized” by one Y ion.

3 A geometrical model

To implement our description, we need a quantitative calculation of α . Noticing XCN in bulk is cubic only on average, a local deformation of the unit cell is expected while substituting one spherical Y ion to the dumbbell-shaped cyanide. Let us then assume local XY unit cell embedded in XCN , to match that of XY in bulk. Such a mechanism yields a local volume deformation of former unit cell of amplitude,

$$\Delta v = \frac{1}{4}(a_{KCN}^3 - a_{KX}^3), \quad (2)$$

(4 molecules per unit cell). Each one of the c Y -nearest neighbours ($c = 12$ on the fcc cyanide sublattice) being affected by these local volume deformations, the overall volume deformation affects on average a total volume $\Delta V = c\Delta v$.

Volume deformation ΔV in turn induces some deformation of neighbouring unit cells. The deformable part of these cells is free volume which originates from volume differences between a given molecule in bulk v_{XCN} and actual molecule itself v_o . We thus have a free volume per molecule,

$$v_f = v_{XCN} - v_o = \frac{a_{XCN}^3}{4} - (v_X + v_{CN}), \quad (3)$$

where a_{XCN} is the pure XCN lattice constant, v_X and v_{CN} are ion volumes [7].

Dumbell-shaped CN reorientations are directly coupled to the unit cell shape via steric hindrance mechanisms. The existence of a finite number of equivalent orientations results from the difference in symmetries between respectively the molecule and the lattice. Symmetry being lower for the molecule, any volume deformation of a cyanide cage (increase or decrease) lowers the corresponding symmetry which in turn disturbs the regular dynamics of cyanide reorientations. More precisely the number of accessible orientations is lowered. Here we are assuming that a cyanide whose cage is deformed (increased or decreased) does not participate in the propagation of long range order at stake in the ferroelastic transition. Accordingly one Y substitution will affect on average,

$$\alpha = c \frac{|\Delta v|}{v_f}, \quad (4)$$

unit cells by deforming their respective free volumes. Along these lines, the effective cyanide density of free-to-reorient cyanides is,

$$x_f = x - \alpha(1 - x). \quad (5)$$

The equality $x_{f,c} = p_c$ yields the critical threshold x_c ,

$$x_c = \frac{p_c + \alpha}{1 + \alpha}. \quad (6)$$

Below x_c a region of randomly oriented ferroelastic domains with no static phase transition is obtained. These domains shrink with increasing dilution to disappear eventually when $x_f = 0$ at a new threshold [8],

$$x_d = \frac{\alpha}{1 + \alpha}. \quad (7)$$

Comparing Eqs. (6, 7) shows it is the non-zero value of p_c which produces the randomly oriented ferroelastic domains. Domains are thus created by site statistical fluctuations. Shear torque experiments [9], as well as diffraction experiments [10] suggested a very similar phase diagram.

Without a fitting parameter direct microscopic calculation of x_c and x_d is readily performed using crystallographic data [11, 12]. The cyanide ion volume is $v_{CN} = 34.47\text{\AA}^3$ [13]. The results are obtained for various mixtures (see the Table) including systems for which no experimental data are available.

4 Dilute random fields

Within the simplest model, cyanide orientations can be represented by ferromagnetic Ising spins $\{S_i\}$. A random site variable ϵ_i is then introduced to account for site dilution. It is one if site i is occupied by a cyanide and zero

otherwise. We have $\{\epsilon_i\}_{av} = x$, where $\{\dots\}_{av}$ denotes a configurational average over site disorder.

Elastic degrees of freedom are also introduced via volume fluctuations to account for the first order character of pure XCN transition. Within an harmonic model they are integrated out to yield an effective Hamiltonian,

$$H_{eff} = -G \sum_{\langle i,j \rangle} \epsilon_i \epsilon_j S_i S_j - E \left(\sum_{\langle i,j \rangle} \epsilon_i \epsilon_j S_i S_j \right)^2, \quad (8)$$

where G and E are constants [14].

With respect to the “neutralization” phenomenon two mechanisms seem possible to block some dipoles in a Y ion vicinity. It could be either a local increase in orientational barriers or the existence of quenched orientational random fields. Local symmetry is the major difference between them. Cubic symmetry is preserved in the first case and not in last. However global cubic symmetry is preserved for both. Available experimental data do not allow actual freezing process to be selected.

Within a two equivalent orientation model, a cyanide prevented from reorientation is indeed trapped along one direction. On this basis, probability p_t to have a local random field is identical to the probability of having a deformed cyanide cage. From the density x_t of trapped cyanide we obtain,

$$p_t = \begin{cases} \frac{\alpha(1-x)}{x} & \text{if } x_d \leq x \leq 1 \\ 1 & \text{if } x < x_d \end{cases}. \quad (9)$$

Associated contribution to the Hamiltonian is,

$$H_t = - \sum_i \epsilon_i h_i S_i, \quad (10)$$

where h_i is a quenched diluted non-symmetry breaking random field. The probability distribution function is,

$$P(h_i) = \frac{p_t}{2} [\delta(h_i - h) + \delta(h_i + h)] + (1 - p_t) \delta(h_i), \quad (11)$$

which satisfies both required symmetry conditions $P(h_i) = P(-h_i)$ and $\overline{h_i} = 0$ where the overline denotes configurational average over the fields. Adding this term to H_{eff} results in full Hamiltonian $H_T = H_{eff} + H_t$ which is rather complicated.

A partial mean field treatment is now performed (more details will be published elsewhere) to extract main physical features of the model. The order parameter is $m = \{\overline{\langle \epsilon_i S_i \rangle}\}_{av}$ where averages are done over both site and random field disorders. The double configurational averaged lattice site free energy is,

$$\begin{aligned} \mathcal{F} = & \frac{1}{2} c G m^2 + \frac{3L}{4} m^4 \\ & - x k_B T \left[\frac{p_t}{2} \{ \ln[\cosh(\beta c G m + \beta L m^3 + \beta h)] + \ln[\cosh(\beta c G m + \beta L m^3 - \beta h)] \} \right. \\ & \left. + (1 - p_t) \ln[\cosh(\beta c G m + \beta L m^3)] \right] - k_B T \ln(2), \end{aligned} \quad (12)$$

where $\beta \equiv \frac{1}{k_B T}$, k_B is the Boltzman constant and T is the temperature. Site and RF disorders have been assumed to be uncorrelated in the averaging, i.e., variables ϵ_i and h_i are statistically independent. The actual value $h_i = h$ or $-h$ is independent of the value of ϵ_i at a given site i . Also, whether $h_i = \pm h$ or 0 does not depend on site i itself. A statistical dependence between h_i and ϵ_i could only results from spatial correlations between CN sites which are anyhow neglected in a MFT.

5 Tricritical points

An exhaustive study of Eq. (12) is out the scope of the present work. At this stage it is useful to analyse two simple limit cases which are physically meaningful. First it is the zero-steric hindrance effect case with $\alpha = 0$. It implies $x_c = p_c$, $x_d = 0$ and $p_t = 0$.

From a Landau expansion of Eq. (12) a continuous transition occurs at the critical temperature, $k_B T_c = xcG$ under the condition of a positive quadratic coefficient,

$$B = -\frac{L}{cG} + \frac{1}{3x^2}, \quad (13)$$

which results in the condition $x < x_L$ on cyanide concentration where,

$$x_L \equiv \left(\frac{cG}{3L}\right)^{1/2}. \quad (14)$$

At $x = x_L$ the continuous transition along $k_B T_c = xcG$ turns first order via a tricritical point ($B = 0$ with a positive free energy sixth order coefficient).

At $x = 1$, $p_t = 0$ (Eq. (9)) even if $\alpha \neq 0$. From experiment, pure XCN exhibits a first order transition. Therefore all plastic systems must satisfy $x_L < 1$ which sets condition $L > \frac{cG}{3}$. Dilution is then found to weaken the first order character of the transition. Associated negative quartic term B gets smaller in amplitude to vanish eventually at a tricritical point ($x = x_L$). There the transition is continuous with tricritical exponents. Upon further dilution the transition becomes second-order for $0 \leq x < x_L$.

6 Results

We now consider the zero-compressibility case ($L = 0$) to study random field effects ($\alpha \neq 0$). At $x = 1$ (no dilution) with p_t an independent external parameter, the zero-compressibility free energy becomes identical to that of trimodal random field Ising models [15, 16, 17] which have been previously studied. A first order transition is found only for $0.73 < p_t \leq 1$ and for some restricted range of random field intensities $\sim 0.55 < \frac{h}{cG} < \sim 0.65$ [17].

These results produce an additional threshold in cyanide density around $p_t = 0.73$ (Eq. (9)),

$$x_r \equiv \frac{\alpha}{0.73 + \alpha}. \quad (15)$$

Only at $x < x_r$ dilution can turn the transition first order via random fields. However condition $x_c < x_r$ must also be satisfied since the transition itself disappears at x_c . The equivalent constraint on α gives,

$$\alpha > \frac{0.73p_c}{1 - 0.73 - p_c} \sim 2.09 . \quad (16)$$

Eq. (22) gives $x_r = 0.60$ and $x_r = 0.83$ for respectively $K(CN)_xBr_{1-x}$ ($\alpha = 1.12$) and $K(CN)_xCl_{1-x}$ ($\alpha = 3.48$). In parallel we found $x_c = 0.62$ and $x_c = 0.82$ for *Br* and *Cl* dilution respectively (see the Table). On this basis we conclude that upon dilution, while random fields can turn the transition first order in $K(CN)_xCl_{1-x}$ mixtures ($x_c < x_r$), they cannot do it for $K(CN)_xBr_{1-x}$ mixtures ($x_c > x_r$).

7 Discussion

It is worth noting that in the vicinity of tricritical points mean field results are indeed reasonable. However, at this stage it is of importance to stress that some doubt exists with respect to the validity of the mean field result of a first order transition for the random field Ising model. A bimodal distribution yields a tricritical point while a Gaussian distribution does not [15, 18, 19, 20].

In parallel Monte Carlo simulations showed a tricritical point to occur in diluted ferromagnets in a staggered field at weak dilution once next nearest interactions are introduced [21]. An exact mapping was earlier found out between the mean field treatment of respectively a bimodal random field and a staggered field [22].

Since our results are in agreement with experiments we have to validate our mean field treatment of a bimodal distribution. This is achieved introducing a staggered symmetry among diluted random fields. It seems to indicate volume deformations may produce staggered random fields.

8 Conclusion

In summary, compressibility and staggered random field are active in making the transition first order. However compressibility weakens with dilution to fade out in the vicinity of x_c for all systems which means it is reasonable to assume $x_L \leq x_c$. On the opposite staggered random fields start to be instrumental at dilution below x_r which has an effect only when $x_r > x_c$, i.e., $\alpha > 2.09$ (Eq. (16)). From the Table this condition is found to be always satisfied except for mixtures with *bromine*.

We can thus predict dilution with *chlorine* and *iodine* keeps the transition first order down to x_c . Only *bromine* turns the transition continuous. A tricritical point is thus expected for $X(CN)_xBr_{1-x}$ mixtures. At this stage our predictions reproduce experimental results with respect to *potassium* systems.

Additional experiments on mixtures with *sodium* and *rubidium* will check the validity of our model.

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Table 1: Numerical values calculated for α , x_c and x_d and experimental thresholds when known (denoted by ‘exp.’). Units for lengths and volumes are Å and Å³. See details in the text. Error bars are within respectively ± 0.01 for all data in the Table, and ± 0.05 for experimental thresholds.

XCN/Y	a_{XCN}	a_{XY}	Δv	v_f	α	x_c	x_d
KCN/Cl	6.53	6.29	7.30	25.19	3.48	0.82 exp: 0.80	0.78 exp: 0.75
KCN/Br	6.57	6.60	2.36	25.19	1.12	0.62 exp: 0.60	0.53 exp: 0.50
KCN/KI	6.53	7.06	18.46	25.19	8.79	0.92 exp: 0.90	0.90
$NaCN/Cl$	5.90	5.65	5.99	12.67	5.68	0.88 exp:~ 0.80	0.86
$NaCN/Br$	5.90	5.97	2.11	12.67	1.99	0.73	0.67
$NaCN/KI$	5.90	6.47	16.63	12.67	15.74	0.95	0.94
$RbCN/Cl$	6.82	6.58	8.05	30.98	3.12	0.80	0.76
$RbCN/Br$	6.82	6.85	1.19	30.98	0.46	0.45 exp: 0.55	0.32